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C09K 3/14 (2006.01)(72) Inventors: **Jimmy Granstrom**, Tualatin, OR (US);
Hisashi Takeda, Tualatin, OR (US)(52) **U.S. Cl.**
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(2013.01); **C09K 3/1409** (2013.01)(73) Assignee: **FUJIMI INCORPORATED**,
Kiyosu-shi (JP)(57) **ABSTRACT**(21) Appl. No.: **17/480,399**

The present technology generally relates to compositions and methods for polishing surfaces comprising a metal and a dielectric film material. Embodiments include methods for polishing a surface comprising W, TEOS/SiO₂ and SiN, comprising applying a polishing slurry comprising an abrasive, a SiN polishing rate enhancer, and an anionic surfactant, and methods of buffering a metal oxide salt in a CMP slurry to obtain an increased robustness against TEOS removal comprising polishing a surface comprising a metal and TEOS by applying a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant.

(22) Filed: **Sep. 21, 2021****Related U.S. Application Data**

(60) Provisional application No. 63/083,461, filed on Sep. 25, 2020.

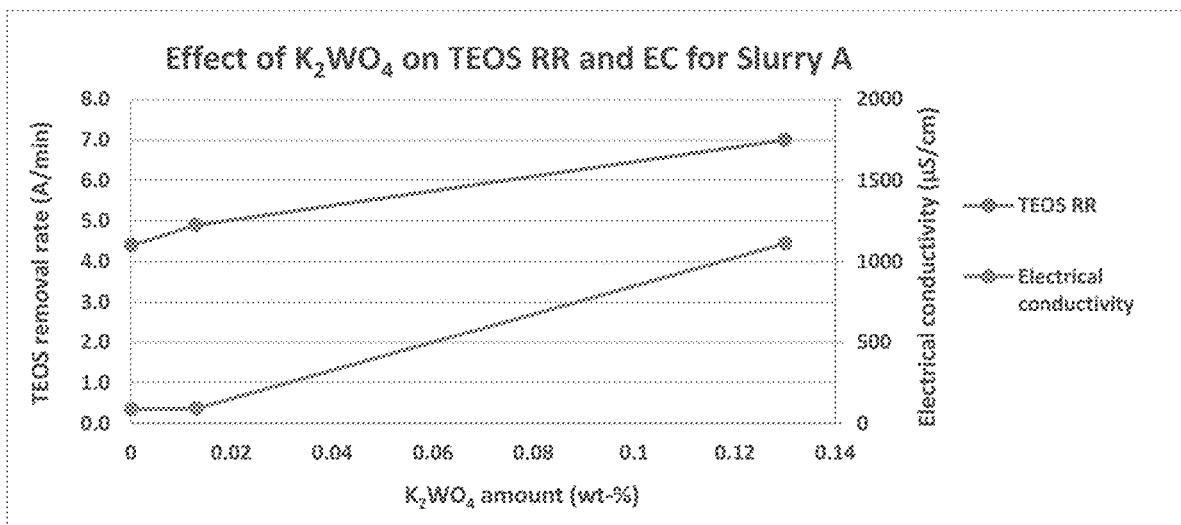


FIGURE 1

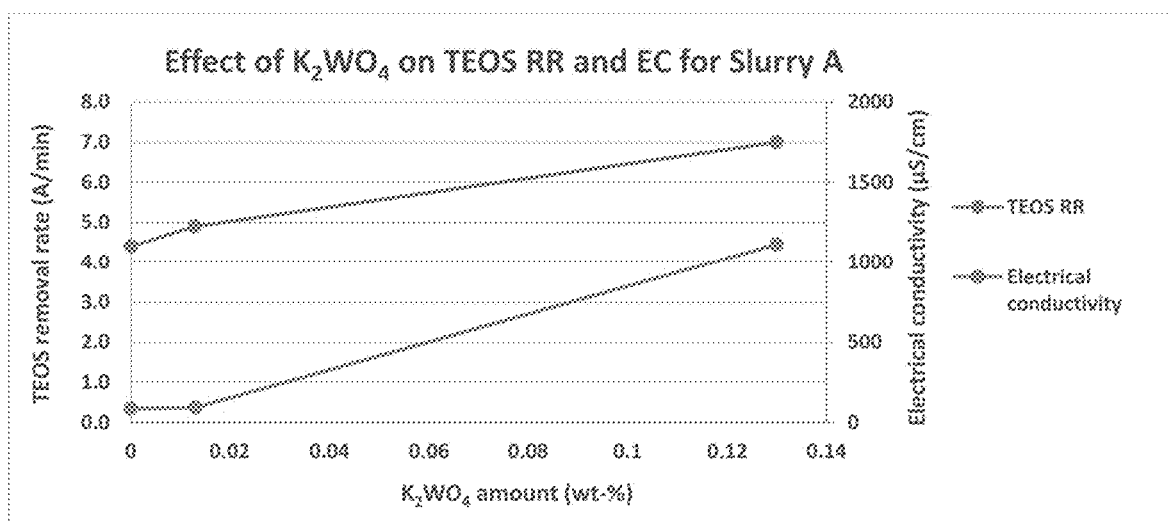
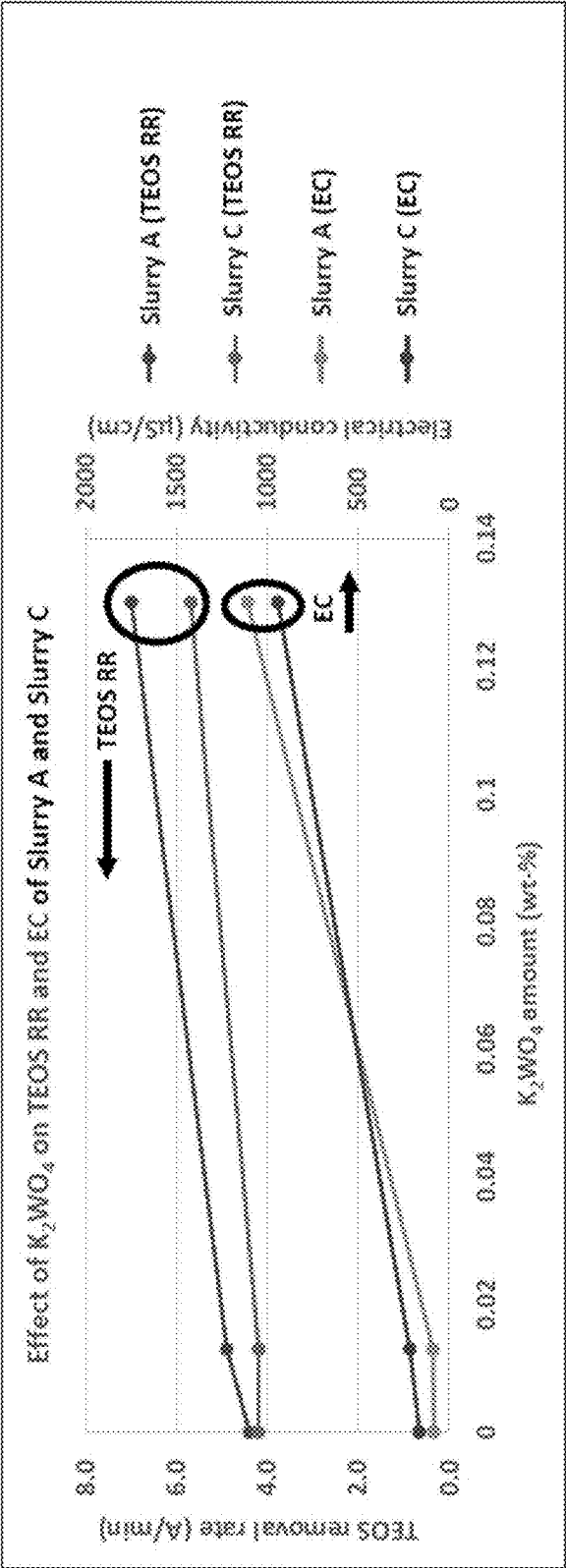


FIGURE 2



CMP SLURRIES

[0001] This application is based on U.S. provisional Patent Application No. 63/083,461 filed Sep. 25, 2020, the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present technology generally relates to compositions and methods for polishing surfaces comprising a metal and a dielectric film material.

BACKGROUND

[0003] Silicon nitride (SiN) chemical mechanical polishing (CMP) slurries are used for a wide range of applications. In addition, tungsten (W) can be part of the patterned wafer.

SUMMARY OF THE DISCLOSURE

[0004] Provided herein are novel compositions and novel methods for polishing surfaces comprising a metal and a dielectric film material.

[0005] Certain aspects of the disclosure include a method for polishing a surface comprising W, TEOS/SiO₂ and SiN, comprising applying a polishing slurry comprising an abrasive, a SiN polishing rate enhancer, and an anionic surfactant. In some embodiments, the abrasive is an anionic modified colloidal silica using sulfonate chemical. In some embodiments, the anionic modified colloidal silica was treated with a sulfonate chemical. In some embodiments, the electrical conductivity value of the polishing slurry is less than 300 μ S/cm. In some embodiments, the electrical conductivity value of the polishing slurry is greater than 100 μ S/cm. In some embodiments, the polishing slurry has a pH of about 4 to about 5. In some embodiments, the SiN polishing rate enhancer is selected from the group consisting of an amino acid and heterocycle carbon compounds. In some embodiments, the anionic surfactant is selected from a sulfonic acid type surfactant. In some embodiments, an amount of SiN polishing rate enhancer is about 0.05 to about 0.5 wt. %. In some embodiments, an amount of abrasive is about 0.8 wt. % or less. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is greater than about 40:1. In some embodiments, the polishing is performed in the presence of WO₄²⁻. Here, TEOS means tetraethyl orthosilicate, and TEOS/SiO₂ indicates that silicon oxide (SiO₂) is a silica oxide film derived from tetraethyl orthosilicate.

[0006] Certain aspects of the disclosure include a method of buffering a metal oxide salt in a CMP slurry to obtain an increased robustness against TEOS removal comprising polishing a surface comprising a metal and TEOS by applying a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant. In some embodiments, the electrical conductivity value of the polishing slurry is less than 300 μ S/cm. In some embodiments, the metal is W and the metal oxide salt includes a WO₄²⁻ anion. In some embodiments, the surface further comprises SiN, and the polishing slurry further comprises a SiN polishing rate enhancer. In some embodiments, the polishing slurry has a pH of about 4 to about 5.

[0007] Certain aspects of the disclosure include a CMP composition comprising an anionic modified colloidal silica abrasive, a SiN polishing rate enhancer, and an anionic

surfactant, wherein the anionic modified colloidal silica abrasive is present in an amount of 1 wt. % or less, and the ratio of abrasive to SiN polishing rate enhancer is within the range of about 1.5 to 1 to about 1.9 to 1. In some embodiments, the CMP composition has a pH of about 4 to about 5. In some embodiments, the SiN polishing rate enhancer is β -alanine.

[0008] Certain aspects of the disclosure include a method for polishing a surface comprising W, TEOS/SiO₂ and SiN, comprising applying a polishing slurry comprising an abrasive, a SiN polishing rate enhancer, and an anionic surfactant, and the electrical conductivity value is 100 μ S/cm to 350 μ S/cm.

[0009] Certain aspects of the disclosure include a method of buffering a metal oxide salt in a CMP slurry to obtain an increased robustness against TEOS removal comprising polishing a surface comprising a metal and TEOS by applying a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant, and the electrical conductivity value is 100 μ S/cm to 350 μ S/cm. Certain aspects of the disclosure include a CMP composition comprising an anionic modified colloidal silica abrasive, a SiN polishing rate enhancer, and an anionic surfactant, wherein the anionic modified colloidal silica abrasive is present in an amount of 1 wt. % or less, and the ratio of abrasive to SiN polishing rate enhancer is within the range of about 1.5 to 1 to about 1.9 to 1, and the electrical conductivity value is 100 μ S/cm to 350 μ S/cm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 shows the effect of K₂WO₄ on TEOS removal rate and electrical conductivity (EC) for a certain CMP composition.

[0011] FIG. 2 shows the effect of K₂WO₄ on TEOS RR and electrical conductivity (EC) for additional specific CMP compositions.

DETAILED DESCRIPTION

[0012] Provided herein are CMP compositions and methods for polishing surfaces comprising a metal and a dielectric film material. As used herein, the term “chemical mechanical polishing” or “planarization” refers to a process of planarizing (polishing) a surface with the combination of surface chemical reaction and mechanical abrasion. In some embodiments, the chemical reaction is initiated by applying to the surface a composition (interchangeably referred to as a ‘polishing (CMP) slurry,’ a ‘CMP composition,’ a ‘polishing composition,’ a ‘slurry composition’ or simply a ‘slurry’) capable of reacting with a surface material, thereby turning the surface material into a product that can be more easily removed by simultaneous mechanical abrasion. In some embodiments, the mechanical abrasion is performed by contacting a polishing pad with the surface and moving the polishing pad relative to the surface.

[0013] Composition

[0014] The CMP polishing compositions disclosed herein can comprise, consist essentially of, or consist of one or more of the following components. Here, “consist essentially of” means that a component not intended to be added to the composition (a component other than the components described below) may be contained in the composition for CMP polishing, for example, up to 0.001% by weight as an upper limit.

[0015] Abrasive

[0016] The CMP compositions of the present disclosure contain at least one abrasive. The abrasive in the CMP composition provides or enhances mechanical abrasion effects during the CMP process. Examples of abrasives that can be used in connection with the present disclosure include but are not limited to alumina abrasive, silica abrasive, ceria abrasive, titanium oxide, zirconia, or mixtures thereof.

[0017] In some embodiments, the abrasive is an anionic modified colloidal silica. In some embodiments, the anionic modified colloidal silica is modified using sulfonate chemical. Thus, in some embodiments, the CMP composition includes anionic modified colloidal silica that includes an anionic group (for example, a sulfonic acid group) bonded to a surface of particles of raw colloidal silica. In some embodiments, anionic modified colloidal silica modified using sulfonate chemicals, for example, can be prepared by method described in "Sulfonic acid-functionalized silica through quantitative oxidation of thiol groups", Chem. Commun. 246-247 (2003). Specifically, silica with sulfonic acid immobilized on the surface can be obtained by coupling a silane coupling agent having a thiol group such as 3-mercaptopropyltrimethoxysilane to silica and then oxidizing the thiol group with hydrogen peroxide.

[0018] The raw colloidal silica can be, for example, colloidal silica produced by a sol-gel method. The production of the raw colloidal silica by a sol-gel method can be performed by using a conventionally known technique, specifically, by using a hydrolyzable silicon compound (for example, an alkoxysilane or a derivative thereof) as a raw material, hydrolysis and condensation reaction is performed, as a result of which the raw colloidal silica can be obtained. The silicon compound may be used singly alone or may also be used in combination of two or more kinds thereof. Further, the raw colloidal silica may also be the one produced by a method other than the sol-gel method. In some embodiments, the average primary particle size of the abrasive is 5 nm or more, 6 nm or more, 7 nm or more, 8 nm or more, 9 nm or more, 10 nm or more, 11 nm or more, 12 nm or more, or 13 nm or more. In some embodiments, the average primary particle size of the abrasive is 33 nm or less, 30 nm or less, 25 nm or less, 20 nm or less, 19 nm or less, 17 nm or less, or 15 nm or less. The average primary particle size of the abrasive may be calculated from the specific surface area of the abrasive grains by the BET method measured using "Flow SorbII 2300" manufactured by Micromeritics Co., Ltd. and the density of the abrasive grains. In some embodiments, the average secondary particle size of the abrasive is 21 nm or more, 23 nm or more, 25 nm or more, 27 nm or more, 29 nm or more, 31 nm or more, or 33 nm or more. In some embodiments, the average secondary particle size of the abrasive is 60 nm or less, 50 nm or less, 45 nm or less, 40 nm or less, 38 nm or less, or 36 nm or less. The average secondary particle size of the abrasive may be calculated by a dynamic light scattering method measured using "Zeta sizer" manufactured by Malvern Panalytical. In some embodiments, the present CMP composition comprises about 0.01% to about 2% by weight of the abrasive. In some embodiments, the present CMP composition comprises less than 2% by weight of the abrasive. In some embodiments, the present CMP composition comprises less than 1% by weight, less than 0.9% by weight, less than 0.8% by weight, less than 0.7% by weight,

less than 0.6% by weight, less than 0.5% by weight, less than 0.4% by weight, less than 0.3% by weight, or less than 0.2% by weight of the abrasive. In some embodiments, the present CMP composition comprises 2% by weight or less, 1.5% by weight or less, 1.2% by weight or less, 1% by weight or less, 0.9% by weight or less, 0.8% by weight or less, 0.7% by weight or less, 0.6% by weight or less, 0.5% by weight or less, 0.4% by weight or less, 0.3% by weight or less, or 0.2% by weight or less of the abrasive. In some embodiments, the present CMP composition comprises 0.01% by weight or more, 0.05% by weight or more, 0.1% by weight or more, 0.3% by weight or more, 0.5% by weight or more, or 0.7% by weight or more.

[0019] SiN Polishing Rate Enhancer

[0020] Certain embodiments of the CMP compositions of the present disclosure contain at least one SiN polishing rate enhancer. In some embodiments, the SiN polishing rate enhancer is selected from the group consisting of an amino acid and heterocycle carbon compounds. In some embodiments, the amino acid is a structure where an amino group is attached to the end of an alkylene group, and a carboxyl group is attached to the opposite end. Non-limiting examples of suitable amino acids include β -alanine and 5-aminovaleric acid. In some embodiments, the alkylene group has 1 to 4, 1 to 3, or 1 or 2 carbon atoms. Non-limiting examples of suitable heterocycle carbon compounds include a heterocycle containing at least one ring nitrogen, e.g., azole, triazole and pyrazine. Specific compounds include 3-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, guanazole or aminopyrazine. Other compounds known to function as a SiN polishing rate enhancer are also included in this disclosure.

[0021] In some embodiments, the present CMP composition comprises about 2% by weight or less of the SiN polishing rate enhancer. In some embodiments, the present CMP composition comprises about 1% by weight or less of the SiN polishing rate enhancer. In some embodiments, the present CMP composition comprises about 0.05 to about 0.5% by weight of the SiN polishing rate enhancer. In some embodiments, the present CMP composition comprises 0.05% by weight or more, 0.06% by weight or more, 0.07% by weight or more, 0.08% by weight or more, 0.09% by weight or more, 0.1% by weight or more, 0.2% by weight or more, 0.3% by weight or more, or 0.4% by weight or more of the SiN polishing rate enhancer. In some embodiments, the present CMP composition comprises 2% by weight or less, 1.5% by weight or less, 1.0% by weight or less, 0.9% by weight or less, less than 0.89% by weight, 0.85% by weight or less, 0.8% by weight or less, 0.7% by weight or less, 0.6% by weight or less, or 0.5% by weight or less of the SiN polishing rate enhancer. In some embodiments, the present CMP composition comprises about 0.1% by weight, about 0.2% by weight, about 0.3% by weight, about 0.4% by weight, about 0.5% by weight, about 0.6% by weight, about 0.7% by weight, about 0.8% by weight, about 0.9% by weight or about 1% by weight of the SiN polishing rate enhancer. The numerical value in this embodiment can be used as the legal basis for the upper limit or the lower limit of the concentration of the SiN polishing rate enhancer. In other words, it is the legal basis or support for amendment. For example, the present CMP composition comprises about 0.2% by weight to about 0.9% by weight, about 0.3% by weight to about 0.8% by weight, or about 0.4% by weight to about 0.7% by weight of the SiN polishing rate enhancer.

[0022] In some embodiments, the abrasive is present in a higher amount than the SiN polishing rate enhancer. In some embodiments, the ratio (the weight ratio) of abrasive to SiN polishing rate enhancer is within the range of about 1.5 to 1 to about 1.9 to 1. For example, in some embodiments, the ratio of abrasive to SiN polishing rate enhancer is about 1.5:1, 1.6:1, 1.7:1, 1.8:1, 1.9:1. In the embodiment, the ratio of abrasive to SiN polishing rate enhancer can be the legal basis for the upper or lower limit of the ratio of abrasive to SiN polishing rate enhancer. In other words, it is the legal basis for amendment. For example, the ratio of abrasive to SiN polishing rate enhancer is about 1.5:1 to 1.7:1, about 1.5:1 to 1.8:1, about 1.5:1 to 1.9:1.

[0023] Anionic Surfactant

[0024] Certain embodiments of the CMP compositions of the present disclosure contain at least one anionic surfactant. In some embodiments, the anionic surfactant is a sulfonic acid type surfactant. For example, ammonium alkyl polyoxyethylene ether sulfates are included by this disclosure. Specific examples include ammonium alkyl polyoxyethylene ether sulfates with nonylphenyl, styrenated phenyl, isodecyl or lauryl alkyl groups. Other compounds known to function as an anionic surfactant in CMP compositions are included by this disclosure. In some embodiments, the anionic surfactant is a sulfonic acid surfactant containing a benzene ring or a naphthalene ring. In some embodiments, the anionic surfactant is alkylbenzene sulfonic acid or a salt thereof, or alkylnaphthalene sulfonic acid or a salt thereof. In some embodiments, the alkyl group contained in the sulfonic acid surfactant has a straight chain or a branched chain. Having a branched chain efficiently leads the desired effect of the present invention. In some embodiments, the sulfonic acid surfactant contains two or more or three or more alkyl groups. In some embodiments, the sulfonic acid surfactant contains 4 or less alkyl groups. In some embodiments, the salt is preferably a sodium salt, an ammonium salt or the like.

[0025] In some embodiments, the present CMP composition comprises about 0.1% by weight or less of surfactant. For example, in some embodiments, the present CMP composition comprises less than 0.01% by weight, less than 0.005% by weight, less than 0.002% by weight, less than 0.001% by weight, less than 0.0009% by weight, less than 0.0008% by weight, less than 0.0007% by weight, less than 0.0005% by weight, less than 0.0004% by weight, less than 0.0003% by weight, or less than 0.0002% by weight of anionic surfactant. The present CMP composition comprises 0.01% by weight or less, 0.005% by weight or less, 0.002% by weight or less, 0.001% by weight or less, 0.0009% by weight or less, 0.0008% by weight or less, 0.0007% by weight or less, 0.0005% by weight or less, 0.0004% by weight or less, 0.0003% by weight or less, or 0.0002% by weight or less of anionic surfactant. In some embodiments, the present CMP composition comprises 0.00005% by weight or more, 0.0001% by weight or more, 0.0002% by weight or more, 0.0003% by weight or more, 0.0004% by weight or more, 0.0005% by weight or more, or 0.0006% by weight or more of surfactant.

[0026] Additional Components

[0027] The liquid carrier of the CMP composition is not particularly limited. In some embodiments, the liquid carrier is water, such as deionized water. The liquid carrier may also be an aqueous solution that has, e.g., an appropriate pH modifier contained therein. In some embodiments, the liquid

carrier can contain one or more organic solvents, such as alcohol compounds, such as fatty alcohols containing 2 to 6 carbon atoms. In some embodiments, the liquid carrier can contain one or more organic solvents, such as glycol ether containing 3 to 10 carbon atoms.

[0028] Examples of aliphatic alcohols with 2 to 6 carbon atoms include ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butanol, pentanol, hexanol, ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, glycerin, 1,2,4-butanetriol, 1,2,6-hexanetriol, erythritol, D-threitol, L-threitol, D-arabinitol, L-arabinitol, ribitol, xylitol, mannitol, and sorbitol. Examples of glycol ethers with 3 to 10 carbon atoms include methyl glycol, methyl diglycol, methyl triglycol, isopropyl glycol, isopropyl diglycol, butyl glycol, butyl diglycol, butyl triglycol, isobutyl glycol, isobutyl diglycol, hexyl glycol, hexyl diglycol, 2-ethylhexyl glycol, 2-ethylhexyl diglycol, aryl glycol, phenyl glycol, phenyl diglycol, benzyl glycol, methylpropylene glycol, methylpropylene diglycol, methylpropylene triglycol, propylpropylene glycol, propylpropylene diglycol, butylpropylene glycol, butylpropylene diglycol, and phenylpropylene glycol. In some embodiments, in the liquid carrier, water is 90% by weight or more, 95% by weight or more, 98% by weight or more, 99% by weight or more, or 99.5% by weight or more.

[0029] In some embodiments, the pH of the CMP composition is a value of from about 3 to about 7. In some embodiments, the pH of the CMP composition is a value of from about 3 to about 6. For example, the pH may be about 4 to about 5. In some embodiments, the pH of the CMP composition is 3 or more, 4 or more, 4.5 or more, or 4.8 or more. In some embodiments, the pH of the CMP composition is less than 7, 6.5 or less, 6.2 or less, 6.0 or less, 5.8 or less, 5.5 or less, 5.3 or less, or 5 or less. Considering the desired effect of the present invention, it is preferable that the pH does not exceed 5. In some embodiments, suitable pH regulators and/or buffers may be included in the composition to adjust the pH. The pH of the CMP composition (liquid temperature: 25° C.) can be confirmed with a pH meter (HORIBA, Ltd. model number: LAQUA). For SiN bulk/buff slurries, one key performance metric is high SiN:TEOS removal rate selectivity to obtain minimum tetraethyl orthosilicate (TEOS) dishing. While at pH 4 there may be W dissolution into WO_4^{2-} (corrosion). If dissolution of the W film occurs during CMP and results in a localized electrical conductivity (EC) increase near an adjacent TEOS structure on a patterned wafer, it potentially affects SiN:TEOS removal rate selectivity and subsequently TEOS dishing. Accordingly, in some embodiments, even if the pH of the CMP composition is particularly 4 or higher, novel CMP compositions that have high dielectric film material (e.g., SiN:TEOS) removal rate selectivity in the presence of a metal, such as W, can be provided. In addition, at pH<4, a passivating WO_3 film can be formed. In some embodiments, the “sweet spot” for SiN:TEOS selectivity may be in the range pH 4 to 5. Thus, in some embodiments, the SiN:TEOS selectivity can be improved even within pH 4 to 5, where there may be an EC increase due to WO_4^{2-} formation. In some embodiments, the metal may not be W, for example, it may be Mo.

[0030] In some embodiments, an acid is used as the pH-adjusting agent. The acid used in connection with the present invention can be organic or inorganic compounds. Examples of the acid include inorganic acids such as sulfuric

acid, nitric acid, boric acid, carbonic acid, hypophosphorous acid, phosphorous acid, and phosphoric acid; and organic acids such as carboxylic acids including formic acid, acetic acid, propionic acid, butyric acid, valeric acid, 2-methylbutyric acid, n-hexanoic acid, 3,3-dimethylbutyric acid, 2-ethylbutyric acid, 4-methylpentanoic acid, n-heptanoic acid, 2-methylhexanoic acid, n-octanoic acid, 2-ethylhexanoic acid, benzoic acid, glycolic acid, salicylic acid, glyceric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, phthalic acid, malic acid, tartaric acid, citric acid, and lactic acid, and organic sulfuric acids including methanesulfonic acid, ethanesulfonic acid, and isethionic acid. Content of the acid in the slurry is not particularly limited as long as it is an amount allowing the slurry to be within the aforementioned pH range.

[0031] In some embodiments, the composition according to the present disclosure may also comprise a biocide or other preservative. Examples of preservatives and biocides that may be used in connection with the present invention include an isothiazoline-based preservative such as 2-methyl-4-isothiazolin-3-one or 5-chloro-2-methyl-4-isothiazolin-3-one, paraoxybenzoate esters, and phenoxyethanol, and the like. These preservatives and biocides may be used either alone or in mixture of two or more kinds thereof.

[0032] In certain embodiments, the electrical conductivity value of the polishing slurry is less than about 300 $\mu\text{S}/\text{cm}$. In certain embodiments, the electrical conductivity value of the polishing slurry is greater than 100 $\mu\text{S}/\text{cm}$. In addition, the electric conductivity of the polishing slurry can be evaluated by a desktop electric conductivity meter (manufactured by HORIBA, Ltd., model number: DS-71). In some embodiments, the electrical conductivity value of the polishing slurry is 400 $\mu\text{S}/\text{cm}$ or less, 380 $\mu\text{S}/\text{cm}$ or less, 360 $\mu\text{S}/\text{cm}$ or less, 340 $\mu\text{S}/\text{cm}$ or less, 320 $\mu\text{S}/\text{cm}$ or less, 300 $\mu\text{S}/\text{cm}$ or less, 280 $\mu\text{S}/\text{cm}$ or less, 260 $\mu\text{S}/\text{cm}$ or less, 240 $\mu\text{S}/\text{cm}$ or less, 220 $\mu\text{S}/\text{cm}$ or less, 200 $\mu\text{S}/\text{cm}$ or less, 190 $\mu\text{S}/\text{cm}$ or less, 180 $\mu\text{S}/\text{cm}$ or less, or 170 $\mu\text{S}/\text{cm}$ or less. In some embodiments, the electrical conductivity value of the polishing slurry is 80 $\mu\text{S}/\text{cm}$ or more, 90 $\mu\text{S}/\text{cm}$ or more, 100 $\mu\text{S}/\text{cm}$ or more, 120 $\mu\text{S}/\text{cm}$ or more, 140 $\mu\text{S}/\text{cm}$ or more, 160 $\mu\text{S}/\text{cm}$ or more, 170 $\mu\text{S}/\text{cm}$ or more, 180 $\mu\text{S}/\text{cm}$ or more, 190 $\mu\text{S}/\text{cm}$ or more, or 200 $\mu\text{S}/\text{cm}$ or more.

[0033] Methods

[0034] In another aspect of the present disclosure, provided herein are methods for CMP of a surface. For example, a method for polishing a surface comprising W, TEOS/SiO₂ and SiN, comprising applying a polishing slurry comprising an abrasive, a SiN polishing rate enhancer, and an anionic surfactant of the embodiments of the present disclosure. Certain embodiments can comprise contacting the surface with a polishing pad; delivering a polishing slurry according to the present disclosure to the surface; and polishing said surface with the polishing slurry. In some embodiments, the polishing is performed in the presence of WO₄²⁻. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is greater than about 40:1. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is greater than 42:1, greater than 44:1, greater than 46:1, or greater than 48:1. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is less than 200:1 or less than 150:1.

[0035] In another aspect of the disclosure, provided herein a method of buffering a metal oxide salt in a CMP slurry to obtain an increased robustness against TEOS removal, comprising polishing a surface comprising a metal (e.g., W, Mo) and TEOS by applying a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant. In addition, robustness will be described in relation to the Table 4 described later. Certain embodiments can comprise contacting the surface with a polishing pad;

delivering a polishing slurry according to the present disclosure to the surface; and polishing said surface with the polishing slurry. In some embodiments, the metal is W and the metal oxide salt includes a WO₄²⁻ anion. In some embodiments, the surface further comprises SiN, and the polishing slurry further comprises a SiN polishing rate enhancer. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is greater than about 40:1. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is greater than 42:1, greater than 44:1, greater than 46:1, or greater than 48:1. In some embodiments, the ratio of SiN removal to TEOS removal during polishing is less than 200:1, or less than 150:1.

EXAMPLES

Example 1: SiN:TEOS Selectivity and W Dissolution

[0036] The effects on SiN:TEOS selectivity and W dissolution for different pH regimes are summarized in Table 1. The trends described in Table 1 apply to the interaction of each wafer type (SiN or TEOS) with particles having a negative zeta potential across the whole pH range (pH 2 to pH 12).

TABLE 1

pH effect on SiN:TEOS selectivity and W dissolution in three pH regimes			
Effect on:	pH < 4	pH 4-5	pH > 5
SiN RR	High RR (large attraction to particle)	Medium RR (attraction to particle)	Low RR (repulsion)
TEOS RR	Medium RR (small attraction to particle)	Low RR (repulsion from particle)	Low RR (repulsion)
W dissolution	WO ₃ passivation → No WO ₄ ²⁻ forms	WO ₄ ²⁻ forms → Higher EC increasing TEOS RR	

[0037] Table 2 shows the ingredients and amounts for slurries in this study, as well as electrical conductivity (EC) values. A higher amount of β -alanine, which is a SiN removal rate enhancer and key element for slurry design, was used for slurries to compensate for their lower abrasive amounts versus Slurry A.

TABLE 2

Measured electrical conductivity (EC) values and ingredients in slurries (all at pH 5 with 0.04 wt. % Triisopropyl-naphthalene sulfonic acid Na salt). Maleic acid was used as pH adjuster.					
Ingredient amount at PoU (wt. %)					
Slurry	Electrical conductivity ($\mu\text{S}/\text{cm}$) at PoU *	Abrasive (Anionic colloidal silica) ^a	β -alanine	Triisopropyl-naphthalene sulfonic acid Na salt	Maleic acid
A	86	1	0.089	0.00066	0.017
B	387	0.75	0.89	0.00066	0.043
C	165	0.75	0.45	0.00066	0.024
D	204	0.75	0.45	0.00066	0.025

^aPrimary particle size: 14 nm; Secondary particle size: 34 nm; The anionic silica has sulfonic acid group on abrasive surface.

[0038] A TEOS removal rate increase caused by a localized EC increase from WO₄²⁻ formation would be due to the contraction of the electrical double layer around the particle, and hence a higher localized TEOS removal rate and potentially higher TEOS dishing on patterned wafers.

[0039] The issue with low TEOS removal rate robustness to WO_4^{2-} can be clearly seen for Slurry A in FIG. 1, showing an increase in TEOS removal rate as the electrical conductivity increases as an increasing amount of K_2WO_4 gets added to the slurry. FIG. 1 shows that K_2WO_4 was intentionally added to slurry A so that the amount of K_2WO_4 is shown on the X-axis of each plot, their electrical conductivity was measured, and the removal rate of TEOS using them under the polishing conditions shown in Table 4 is shown on the Y-axis. An elevated K_2WO_4 amount is believed to simulate the high WO_4^{2-} chemical environment for TEOS near W on patterned wafers at $\text{pH} \geq 4$.

[0040] In order to evaluate the effect of W polishing on TEOS removal rate, an experimental polishing procedure was designed for W and TEOS blanket test wafers (blanket wafers), see Table 3. The experimental procedure aims to simulate the localized increase in WO_4^{2-} for TEOS lines near W lines on patterned wafers.

[0041] Two blanket wafers were prepared as a first wafer and a second wafer. In addition, ex-situ conditioning was performed to process the pads. After polishing the first wafer using the pad, the second wafer was polished. No conditioning was performed between the polishing of the first wafer and the polishing of the second wafer. For example, after polish of the first wafer, high pressure rinse with deionized water or pad conditioning was not performed. By doing so, TEOS removal rates were determined after the second polish.

[0042] More specifically, the TEOS blanket wafer was polished with Slurry A for 8 minutes using a pad subjected to ex-situ conditioning. Subsequently, the Slurry A was used to polish another TEOS blanket wafer for 4 minutes ("a") in Table 3, 8 minutes TEOS/4 minutes TEOS). At this time, the pad cleaning or conditioning step was not performed between the polishing of each wafer.

[0043] In addition, the W blanket wafer was polished with Slurry A for 8 minutes using a pad subjected to ex-situ conditioning. Subsequently, the TEOS blanket wafer was polished for 4 minutes using the Slurry A ("b") in Table 3, 8 minutes W/4 minutes TEOS). At this time, the pad cleaning and conditioning step was not performed between the polishing of each wafer.

[0044] Table 3 briefly summarizes the procedure and purpose of the above experiment. The point of this experiment is that the pad cleaning and conditioning steps were not performed between the polishing of each wafer. By not performing such cleaning and conditioning, the pad after polishing the first wafer contains a product derived from the

first wafer. That is, regarding b) 8-minute W/4-minute TEOS, the first wafer-derived product contains W (including the dissolved form of W) and the like, and by polishing the TEOS blanket wafer with a pad containing the W (including the dissolved form of W) and the like, the influence of W (including the dissolved form of W) and the like on TEOS can be evaluated.

TABLE 3

Runs and wafers used for the experimental procedure to check the effect of W polishing on TEOS RR for the slurries in Table 2.			
Run	blanket wafer #1	blanket wafer #2	Purpose
a) 8 min. TEOS/4 min. TEOS (ex-situ)	8 min. TEOS	4 min. TEOS	Reference. Check the effect of no W polishing on TEOS RR
b) 8 min. W/4 min. TEOS (ex-situ)	8 min. W	4 min. TEOS	Check the effect W polishing on TEOS RR

[0045] FIG. 2 shows the effect of K_2WO_4 on TEOS removal rate and electrical conductivity (EC) for additional specific CMP compositions. More specifically, FIG. 2 shows that K_2WO_4 was intentionally added to slurry A and slurry C respectively so that the amount of K_2WO_4 are shown on the X-axis of each plot, and their electrical conductivity was measured, and the removal rate of TEOS using them under the polishing conditions shown in Table 4 is shown on the Y-axis.

[0046] As can be seen in FIG. 2, if TEOS removal rate of a slurry has a low robustness to W polishing (i.e. it is more strongly affected by WO_4^{2-} in run b)), it would be expected that run b is supposed to exhibit a higher TEOS RRs (blanket wafer #2) than run a). In other words, the same or similar TEOS RRs (blanket wafer #2) for runs a) and b) may be indicative of a greater robustness against WO_4^{2-} caused by W polishing, and potentially a lower TEOS dishing on patterned wafers. That is, the fact that the removal rates of 8 minutes TEOS/4 minutes TEOS (ex-situ) and 8 minutes W/4 minutes TEOS (ex-situ) are the same means that TEOS has a greater robustness against WO_4^{2-} .

TABLE 4

Slurry ingredient ratios versus 200 mm TEOS removal rates as a function of W polishing (ex-situ conditioning) or 200 mm blanket removal rates during regular polishing operation (in-situ conditioning).						
Slurry	200 mm TEOS blanket wafer removal rate (A/min) * as a function of W polishing **		Robustness evaluation	200 mm in-situ blanket wafer RRs (A/min) *, ***		
	8 min. TEOS/4 min. TEOS (ex-situ)	8 min. W/4 min. TEOS (ex-situ)		SiN	TEOS	TEOS/SiN removal rate selectivity (—)
A	4.7	6.1	1.4	206	6	34
B	7.9	8.8	0.9	288	8	36

TABLE 4-continued

Slurry ingredient ratios versus 200 mm TEOS removal rates as a function of W polishing (ex-situ conditioning) or 200 mm blanket removal rates during regular polishing operation (in-situ conditioning).						
Slurry	200 mm TEOS blanket wafer removal rate (Å/min) * as a function of W polishing **		Robustness evaluation	200 mm in-situ blanket wafer RRs (Å/min) *, ***		
	8 min. TEOS/4 min. TEOS (ex-situ)	8 min. W/4 min. TEOS (ex-situ)		SiN	TEOS	TEOS/SiN removal rate selectivity (—)
C	4.9	4.3	0.6	247	5	49
D	4.6	4.3	0.3	260	5	52

* Polishing condition: 1.5 psi (polishing pressure) -63 rpm (rotation speed) -125 ml/min (slurry supply speed) -IC1010 (polishing pad) -A165-Westech (200 mm) (polishing equipment name for polishing 200 mm wafers).

** W polishing effect experiment: Two wafers were polished with ex-situ pad conditioning for each run, with no high pressure rinse with deionized water or pad conditioning after polish of the first wafer. TEOS removal rate were determined after the second polish.

*** Polish times: 1 minute for SiN, 4 minutes for TEOS and W. In-situ conditioning for all runs.

[0047] Table 4 shows TEOS removal rates using the experimental procedure shown in Table 3. In order for a SiN bulk/buff slurry to be considered robust (having a robustness) and efficient, the two requirements below could be fulfilled.

[0048] 1) No significant increase in TEOS removal rate with longer W polishing times. That is, the absolute value of the difference between (a) and (b) is less than 0.9. Therefore, in one embodiment, “increased robustness” means that the difference of the absolute value between (a) and (b) (also referred to as robustness value) is less than 0.9, 0.8 or less, 0.7 or less, or 0.6 or less.

[0049] 2) A SiN/TEOS selectivity >40.

[0050] In one embodiment of the present invention, a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant, and the electric conductivity value is 100 $\mu\text{S}/\text{cm}$ to 350 $\mu\text{S}/\text{cm}$, and the robustness value is 0.9 or less, is provided.

[0051] As can be seen in table 4, Slurry C and Slurry D fulfill both of the requirements above. It appears that there is an amount of β -alanine (or slurry EC) that is ideal in order to maintain TEOS removal rate robustness against W polishing.

[0052] Table 5 shows that K_2WO_4 was intentionally added (spike) to the slurries A and C so that the concentrations are shown in Table 2, and the respective electric conductivity and TEOS RRs were measured, and the results are shown. In addition, the polishing conditions in Table 5 are as shown in Table 4.

[0053] As can also be seen in Table 5, the increase in EC and TEOS removal rate with K_2WO_4 spike is significantly lower for Slurry C compared with Slurry A. A 0.13 wt. % K_2WO_4 spike (equivalent to a 1000 ppm WO_4^{2-}) results in a 13 \times increase of EC for Slurry A but only a 5.7 \times increase for Slurry C, hence Slurry C enables an almost 2 \times reduction in EC increase compared with Slurry A. Consequently, the TEOS removal rate increase Slurry C is significantly lower (1.4 \times) compared with the TEOS removal rate increase for Slurry A (1.6 \times) at 0.13 wt. % K_2WO_4 (1000 ppm WO_4^{2-}).

[0054] Table 5 helps to demonstrate the improved WO_4^{2-} buffering capacity of Slurry C compared with Slurry A. An EC increase of 5.7 \times (Slurry C) after exposure to 1000 ppm WO_4^{2-} enables a significantly lower TEOS removal rate increase compared with an EC increase of 13 \times (Slurry A). The data suggests that a significant difference in TEOS removal rate response should be expected within the K_2WO_4 range 0.013-0.13 wt. %, suggesting a wider TEOS removal rate robustness window for Slurry C versus Slurry A.

TABLE 5

Slurry ingredient amounts and effect of K_2WO_4 amount on EC and TEOS removal rate.						
Slurry	K_2WO_4 spike		Electro conductivity		TEOS Removal rate	
	K_2WO_4 (wt %)	Equivalent to WO_4^{2-} amount (ppm)	$\mu\text{S}/\text{cm}$	Normalized EC*	$\text{\AA}/\text{min}$	Normalized Removal rate*
A	0	0	86	1.0	4.4	1.0
	0.013	100	165	1.9	4.9	1.1
	0.13	1000	1112	13	7.0	1.6
C	0	0	165	1.0	4.2	1.0
	0.013	100	217	1.3	4.2	1.0
	0.13	1000	944	5.7	5.7	1.4

*(Value for slurry with K_2WO_4 spike)/(Value for slurry without K_2WO_4 spike). K_2WO_4 -free slurry = 1.0.

[0055] The other important parameter for TEOS removal rate robustness against W polishing is abrasive amount. In some embodiments, the slurry may contain a W corrosion inhibitor (e.g., a nitrogen-containing W corrosion inhibitor such as benzotriazole).

EQUIVALENTS

[0056] The present technology is not to be limited in terms of the particular embodiments described in this application, which are intended as single illustrations of individual aspects of the present technology. Many modifications and variations of this present technology can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the present technology, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the present technology. It is to be understood that this present technology is not limited to particular methods, reagents, compounds compositions, or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0057] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0058] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 items refers to groups having 1, 2, or 3 items. Similarly, a group having 1-5 items refers to groups having 1, 2, 3, 4, or 5 items, and so forth.

[0059] All numerical designations, e.g., pH, temperature, time, concentration, amounts, and molecular weight, including ranges, are approximations which are varied (+) or (−) by 10%, 1%, or 0.1%, as appropriate. It is to be understood, although not always explicitly stated, that all numerical designations may be preceded by the term “about.” As used herein, the term “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art given the context in which it is used, “about” will mean up to plus or minus 10% of the particular term. It is also to be understood, although not always explicitly stated, that the reagents described herein are merely exemplary and that equivalents of such are known in the art.

[0060] All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification. Other embodiments are set forth in the following claims.

1. A method for polishing a surface comprising W, TEOS/SiO₂ and SiN, comprising applying a polishing slurry comprising an abrasive, a SiN polishing rate enhancer, and an anionic surfactant, and an electrical conductivity value is 100 μS/cm to 350 μS/cm.

2. The method of claim 1, wherein the abrasive is an anionic modified colloidal silica using sulfonate chemical.

3. The method of claim 2, wherein the anionic modified colloidal silica was treated with a sulfonate chemical.

4. The method of claim 1, wherein the electrical conductivity value of the polishing slurry is less than 300 μS/cm.

5. The method of claim 1, wherein the electrical conductivity value of the polishing slurry is greater than 100 μS/cm.

6. The method of claim 1, wherein the polishing slurry has a pH of about 4 to about 5.

7. The method of claim 1, wherein the SiN polishing rate enhancer is selected from the group consisting of an amino acid and heterocycle carbon compounds.

8. The method of claim 1, wherein the anionic surfactant is selected from a sulfonic acid type surfactant.

9. The method of claim 1, wherein an amount of the SiN polishing rate enhancer is about 0.1 to about 0.8 wt. %.

10. The method of claim 1, wherein an amount of abrasive is about 0.8 wt. % or less.

11. The method of claim 1, wherein the ratio of SiN removal to TEOS removal during polishing is greater than about 40:1.

12. The method of claim 1, wherein the polishing is performed in the presence of WO₄^{2−}.

13. A method of buffering a metal oxide salt in a CMP slurry to obtain an increased robustness against TEOS removal comprising polishing a surface comprising a metal and TEOS by applying a polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant, and an electrical conductivity value is 100 μS/cm to 350 μS/cm.

14. The method of claim 13, wherein the electrical conductivity value of the polishing slurry is less than 300 μS/cm.

15. The method of claim 13, wherein the metal is W and the metal oxide salt includes a WO₄^{2−} anion.

16. The method of claim 13, wherein the surface further comprises SiN, and the polishing slurry further comprises a SiN polishing rate enhancer.

17. The method of claim 13, wherein the polishing slurry has a pH of about 4 to about 5.

18. A CMP composition comprising an anionic modified colloidal silica abrasive, a SiN polishing rate enhancer, and an anionic surfactant, wherein the anionic modified colloidal silica abrasive is present in an amount of 1% by weight or less, and the ratio of the abrasive to the SiN polishing rate enhancer is within the range of about 1.5 to 1 to about 1.9 to 1, and

an electrical conductivity value 100 μS/cm to 350 μS/cm.

19. The CMP composition of claim 18, wherein the CMP composition has a pH of about 4 to about 5.

20. The CMP composition of claim **18**, wherein the SiN polishing rate enhancer is β -alanine.

21. A polishing slurry comprising an anionic modified colloidal silica abrasive and an anionic surfactant, an electrical conductivity value is 100 $\mu\text{S}/\text{cm}$ to 350 $\mu\text{S}/\text{cm}$, and a robustness value is 0.9 or less.

* * * * *